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(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS AND APPARATUS FOR THE THERMAL CRACKING OF
HEAVY OILS WITH A FLUIDIZED PARTICULATE HEAT CARRIER

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The present invention relates to a process and apparatus for the thermal cracking of heavy hydrocarbon oils, such as crude oil, topped crude oil, fuel oil, reduced pressure residual oil, tar sand oil, pitch, asphaltene and the like (hereinafter referred to as "heavy oils"). More particularly, the invention relates to a process and apparatus for the thermal cracking of heavy oils wherein a heavy oil is fed to a reactor, in which a fluidized bed of a particulate heat carrier is maintained, and thermally cracked at a temperature of 700°C to 850°C in the presence of steam to produce olefins, for example, ethylene. The invention is concerned with a process and apparatus wherein a cyclone dust collector and a gravitational separator are jointly used to recover the particles of the heat carrier which have escaped from the top of the reactor.

A process for the production of olefins wherein a crude oil, various residual oils and other heavy oils are thermally cracked by means of a fluidized bed of a particulate heat carrier, has been described in Japanese Patent Publication No. 36,289/1970.

The known apparatus for carrying out such processes are generally provided with a cyclone dust collector in order to reduce the loss of the particulate heat carrier. Most of the particles of the heat carrier, which have been accompanied by a stream of the reaction product and escape from the reactor may be collected by the cyclone and returned to the fluidized bed.

In the thermal cracking of heavy oils, carbonaceous materials are normally by-produced to a great extent. Almost all of this carbonaceous material will deposit onto the particles of the heat carrier in the reactor, while the remaining portion will leave the fluidized bed. In the thermal cracking of heavy oils, the amount of carbonaceous material leaving the fluidized bed is larger than that in the thermal cracking of lighter oils.

and unavoidably such carbonaceous materials are deposited and accumulate on the walls of various parts, of the apparatus, located along the path between the reactor and a device for quenching the thermally cracked product. This deposition and accumulation of carbonaceous material is especially remarkable when the process is carried out at high temperatures as is the case with the process of the invention. For the purpose of producing olefins at temperatures as high as 700°C to 850° must be maintained in the reactor.

10 Once such deposition of carbonaceous materials (generally referred to as "coking") has occurred on the inside walls of the cyclone, protrusions and depressions are formed on the inner surfaces of the walls, which disturb the flow of gases in the cyclone and prevent solid particles which are to be collected by the cyclone from smoothly moving along the inner walls of the cyclone. Thus, the dust collecting ability of the cyclone is lowered to a great extent. On the other hand, in the thermal cracking of heavy oils for producing olefins, high
20 temperatures must be maintained in the reactor and at the same time the process must be carried out with the residence time of the cracked products in the reactor as short as possible, otherwise the products are excessively cracked to produce products of low value.

 To realize the desired short residence time, the reactor must be operated with the highest possible linear velocity of gas in the fluidized bed and with the smallest possible space above the fluidized bed. As a result, on the one hand the fluidized state of the particles in the bed is so vigorous and non-uniform, that short period pressure variations of significant size occur in the reactor and on the other
30 hand the interface between the fluidized bed and the space above the bed approaches the exit of the reactor so that the

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buffering function of the space is reduced. Consequently, the behavior of particles and the disturbance of gas in the fluidized bed directly affect the cyclone in that variations in pressure difference between the bottom of the cyclone and the lower end of a duct for returning collected particles to the reactor, become large, and the amount of gas flowing up through the duct to the cyclone increases. These factors, in addition to the above-discussed coking, further lower the dust collecting ability of the cyclone.

10 As discussed above, in a process for producing olefins by thermally cracking heavy oils with a fluidized bed carrier, the dust collecting ability of the cyclone, is inevitably lowered with time owing to the required high temperature and short residence time. Accordingly, as compared with other processes using a similar fluidized heat carrier under different conditions, the amount of the particles of the heat carrier which escape the reactor, without being collected by the cyclone and which pass to the processing stage for reaction products, is large, resulting in frequent problems in operation.

20 As the particulate heat carrier, there may suitably be employed such materials as particulate coke, sand and finely divided ceramics. The particles of the heat carrier forming the fluidized bed may be classified in two classes, one class comprising coarse particles having a diameter such that they may readily be collected by a cyclone, while the other class comprises fine particles having a diameter such that they are inherently difficult to collect by a cyclone. The particles of the heat carrier, which are passed to the processing stage for the reaction products are mainly composed of the above-mentioned fine particles and a portion of the above-mentioned
30 coarse particles having a diameter which is small as compared with the remainder of the coarse particles. Thus the

particles of the heat carrier remaining in the reactor are of relatively large size. Further, the deposition of cracked coke onto the particles make them larger still. As a result, the fluidized state in the bed becomes intolerably non-uniform, and pressure variations in the reactor become large. These changes with time make it difficult to operate the apparatus smoothly. Furthermore, when the reactor comprises heating and reaction columns, through which the fluidized heat carrier is recirculated, a smooth recirculation of particles between these columns is prevented if the particles in the fluidized bed become excessively large.

In addition to the above-discussed problems, the following difficulties occur with respect to the material balance of the particulate heat carrier in the fluidized bed. In a reactor for thermally cracking heavy oils with the fluidized particulate heat carrier, while coke is produced in the fluidized bed by the thermal cracking of heavy oils, the particles of the heat carrier are pulverized by the impingement and friction of the particles against each other and with the walls of the reactor, and the resultant fine particles may be withdrawn from the reactor in a stream of the reaction product. Particularly, when a particulate coke is used as a heat carrier, loss of heat carrier occurs partly due to the gasification of the particulate coke by reaction with steam in the reactor and partly due to a lowering in the dust collecting ability of the cyclone located at the exit of the reactor. As already discussed, the dust collecting ability of the cyclone is progressively lowered with time. As loss of coarse particles of coke due to lowering in the dust collecting ability of the cyclone increases, the total loss of coke eventually exceeds an amount of coke produced even in the case where a heavy oil, which is likely to form an amount of coke, is used as a

feed oil, and thus, it becomes necessary to supplement the reactor with an additional amount of particulate coke in order to maintain the required volume in the fluidized bed.

In order to cope with these circumstances, a quantity of the particulate heat carrier must frequently be withdrawn from the fluidized bed, pulverized, sieved and then returned to the bed in order to prevent the size of particles in the bed from becoming excessively large; a fresh particulate heat carrier in an amount to compensate for the loss thereof must be added
10 to the fluidized bed, and, in order to prevent fine and coarse particles of the heat carrier, which have passed to the processing stage for the reaction product, from depositing in parts along the path of the cracked oil and, thus, causing troubles in operation, these particles of the heat carrier must be separated from the cracked oil and further processed. However, it is not only extremely troublesome but also economically quite disadvantageous to frequently carry out the withdrawal, pulverization and returning of particles and the supplementing of fresh particles.

20 As already stated, the known apparatus is generally provided with a cyclone at the exit of the reactor in order to recover the solid particles suspended in a stream of the reaction product. The primary object of providing the cyclone is to prevent loss of particles as well as to prevent the reaction product from being contaminated with particles of the heat carrier suspended therein. Accordingly, in the prior art, fine particles of the heat carrier, which have not been collected by the cyclone, are separated from the reaction product as follows. The reaction product containing fine particles of
30 the heat carrier is quenched to provide a cracked oil containing the particles of the heat carrier suspended therein; the oil is fractionated in a vacuum distillation column; and, finally

the resultant relatively high boiling oil containing the particles of the heat carrier is processed by means of a centrifuge or filter to remove the solid particles. However, some of the particles suspended in the reaction product are so fine that it is difficult to completely remove them from the oil, further the treatment of separated particles is troublesome since they are wetted with cracked oil.

The present invention seeks to provide a solution to the above-mentioned problems normally involved in a process for the thermal cracking of heavy oils with a fluidized particulate heat carrier.

The invention further provides a process for the thermal cracking of heavy oil in which an improvement in the material balance of the particulate heat carrier and the desirably small change with time of particle size distribution of the particulate heat carrier can be achieved and which can be continuously carried out for a prolonged period of time under substantially constant conditions.

The invention further provides a process for the thermal cracking of heavy oils in which coking onto inner walls of the cyclone and its duct for returning collected particles to the reactor can be substantially eliminated or reduced and which may be carried out while maintaining a high level of the dust collecting ability of the cyclone.

The invention further provides apparatus for the process of the invention.

It has now been found that if the process for the thermal cracking of heavy oils with a fluidized particulate heat carrier is carried out while recovering particles of the heat carrier in a stream of the reaction product by means of a cyclone and a gravitational separator, returning the particles of the heat carrier recovered by the cyclone directly to the reactor and returning the particles of the heat carrier recovered

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by the gravitational separator to the reactor in the form of suspension in a cracked oil, an improvement in the balance of the particulate heat carrier and a desirably small change with time of particle size distribution of the particulate heat carrier can be achieved so that the process may be continuously carried out for a prolonged period of time under substantially constant conditions.

Thus, according to the invention there is provided in a process for the thermal cracking of heavy oils with a fluidized bed of a particulate heat carrier comprising forming
10 a fluidized bed of a particulate heat carrier with a heavy oil and steam in a reactor and thermally cracking said heavy oil at a temperature of about 700°C to about 850°C, the improvement wherein a major proportion of the particles of the heat carrier contained in a stream of the reaction product, is recovered with a collector for collecting particles of the heat carrier and returned to said fluidized bed; the remainder of the particles of the heat carrier contained in said stream, and which are not recovered by said collector, and which are passed to a processing
20 stage for the reaction product, being allowed to settle under gravity in a cracked heavy oil; said cracked heavy oil being separated into two portions, a first portion containing relatively coarse particles of the heat carrier suspended therein and a second portion containing relatively fine particles of the heat carrier suspended therein; and said first portion of the cracked heavy oil, containing relatively coarse particles of the heat carrier suspended therein, is returned to said fluidized bed.

It has also been found that when carrying out the
30 process of the invention, if the cyclone is located outside the thermal cracking reactor, and the particles of the heat carrier collected by the cyclone are returned to the reactor

at a position which is below the position where the heavy oil is fed to the reactor, coking onto the inner walls of the cyclone and its dust for returning collected particles to the reactor is eliminated or greatly reduced so that the process can be carried out for a prolonged period of time without suffering from an undesirable lowering of the dust collecting ability of the cyclone.

10 If desired, the coarse particles of the heat carrier suspended densely in the cracked heavy oil, can be washed with a light oil and then returned to the fluidized bed. By doing so, the particles of the heat carrier which are wetted with the cracked heavy oil and which are rather sticky, can be converted to particles which are not sticky and which can be readily handled.

According to another aspect of the invention there is provided apparatus for the thermal cracking of a heavy oil to produce olefins comprising:

- 20 (i) a cracking reactor adapted to maintain a fluidized bed of a particulate heat carrier including first inlet means in a lower portion for steam, second inlet means for feeding heavy oil to said reactor and first outlet means in an upper portion for cracked product,
- (ii) first conduit means communicating said first outlet means with a cyclone adapted to separate a major portion of particulate heat carrier in said cracked product, and second outlet means in said cyclone for separated heat carrier particles,
- 30 (iii) second conduit means communicating said second outlet means with a third inlet means in said cracking reactor,
- (iv) fourth outlet means in said cyclone and third conduit means communicating said fourth outlet means

with separating means including settling means for settling coarse particles of heat carrier contained in said cracked product.

- (v) fifth outlet means in said settling means and fourth conduit means communicating said fifth outlet means with fourth inlet means in said cracking reactor for return of cracked product containing said coarse particles of heat carrier, and
- (vi) sixth outlet means in said settling means for cracked product containing fine particles of heat carrier.

10

The invention will be further described in its preferred embodiments with reference to the attached drawings in which:

FIGURE 1 is a flow chart schematically illustrating an apparatus for carrying out the process of the invention and;

FIGURE 2 is an enlarged vertical cross-sectional view showing a reaction column and a cyclone in the apparatus of FIGURE 1.

- 20 A specific form of the invention is further described with reference to FIGURE 1.

A thermal cracking reactor 1 utilizing a fluidized bed of a particulate heat carrier is maintained at a temperature ranging between 700°C and 850°C. The particulate heat carrier is fluidized by blowing steam into the reactor through nozzles 2, 3 provided at a lower part of the reactor, and a feed oil to be processed is fed into the fluidized bed through a nozzle 4.

- 30 In the reactor the feed oil is thermally cracked to produce a cracked gas and oil as well as carbonaceous materials. Almost all or a major part of the carbonaceous materials deposits on the surfaces of the particles forming the fluidized bed of the heat carrier.

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The cracked gas and a vapor of the cracked oil is passed through a conduit 5 to a cyclone 6 where most of the particles of the heat carrier contained in the gaseous stream from the reactor 1 are separated from the stream and then returned through a conduit 8 to the reactor 1.

Partly because of a lowering of the gas-solid separating ability of the cyclone 6 due to deposition of the carbonaceous materials, formed by the thermal cracking, onto the inner surfaces of the cyclone 6 and partly for other reasons including a possible back flow of gas from the conduit 8, a part of the relatively coarse particles of the heat carrier, which are normally to be collected by cyclone 6 is discharged through a conduit 7 to a quenching device 9 together with the cracked gas in the form of a vapor of the cracked oil and fine particles of the heat carrier incapable of being collected by the cyclone 6. The mixture is quenched in the device 9 to a temperature of 150°C to 350°C by spraying with oil and then passed through a pipe 10 to a distillation column 11 which is operated at normal pressure.

A mixture of the cracked gas and a fraction of the oil having a boiling point below 170°C or 230°C, is passed from the top of the distillation column 11 to the subsequent processing steps. The remaining fraction of the oil boiling at higher temperatures provides a liquid containing fine and coarse particles of the heat carrier, and is passed through a duct 13 to a gravitational separator 14 by its own weight or by a suitable pressure difference between the column 11 and the separator 14 (without passing through any mechanical device). In the gravitational separator 14, which is maintained at a relatively high temperature, the difference in specific gravity between the oil and the solid heat carrier is significant and the viscosity of the oil is low. Accordingly, if the separator

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14 is operated with a low rate of flow or a long residence time, coarse particles of the heat carrier readily settle down and accumulate at the bottom of the separator 14, whereby an oil containing 5 to 40% by weight of coarse particles of the heat carrier suspended therein and an oil containing only fine particles of the heat carrier may be separated. If desired, the distillation column 11 may be constructed so that the bottom portion of the column 11 may itself serve as a gravitational separator.

10 Coarse particles of the heat carrier suspended in the cracked oil are withdrawn from the gravitational separator 14 at the bottom thereof and are recycled through a duct 18 and a nozzle 19 to the reactor 1, where they are re-used as the particles forming the fluidized bed.

Accordingly, the loss of coarse particles can be eliminated and the change in particle size distribution in the fluidized bed with time is slight. The oil, from which coarse particles of the heat carrier have been separated, is withdrawn from the separator 14 through a pipe 15. A
20 major portion of the oil is to be recycled to the quenching device 9, and is passed through a pipe 16 to a heat exchanger 17, where it is cooled and then returned through a pipe 21 to the quenching device 9. Since the oil is free from coarse particles of the heat carrier, an oil spraying nozzle in the quenching device 9, the heat exchanger, flow control valve, pump for regulating a flow rate of oil, and flow meter do not suffer by being clogged due to deposition of coarse particles. The rest of the oil from separator 14 is passed through a pipe
20 to subsequent processing steps.

30 The heat required for the thermal cracking of the heavy oil is supplied to the particulate heat carrier maintained in a fluidized state in a heating column 22. The fluidized

heat carrier is recirculated through the heating column 22 and reaction column 1 via ducts 23 for transporting particles of the heat carrier. The heating may be effected by burning a suitable fuel, such as carbonaceous materials, fuel oil or fuel gas, in the heating column 22. The flue gas is withdrawn from the heating column 22 through a duct 24.

In the process of the invention, even in the case where appreciable amounts of the particles of the heat carrier are not collected by the cyclone 6, located at the exit of the reaction column 1, due to lowering in its efficiency, and are passed to the stage of processing the reaction product, it is not necessary to isolate completely the particles of the heat carrier from the by-produced cracked oil. Accordingly, it is possible in the process of the invention to utilize gravitational separation, which is the simplest and most reliable method of separating coarse particles of the heat carrier. Furthermore, other separating means, such as centrifuges and filters, are not necessary for carrying out the process of the invention, and thus, the process of the invention is completely free from mechanical troubles which occur when employing such means.

In the gravitational separator 14, coarse particles of the heat carrier may readily be settled in the cracked oil, so far as they have a particle size of at least 0.15mm, by continuously introducing the cracked oil containing those particles suspended therein to the gravitational separator 14 comprising a vessel, while controlling the flow rate of liquid in the vessel to a rate substantially less than the terminal velocity of the particles.

The settling of the particles may be facilitated by lowering the viscosity of the oil or by raising the temperature of the oil. The coarse particles of the heat carrier,

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which settle in the gravitational separator 14, may be withdrawn from the separator 14 at the bottom thereof as a dense suspension in the cracked oil. By recycling the suspension, all the coarse particles of heat carrier coming from the fluidized bed may be returned to the reactor, ensuring the minimum loss of the particulate heat carrier as well as the prevention of loss of coarse particles.

Accordingly, any change in the average particle size and particle size distribution of the particles of heat carrier with time which renders them unsuitable for proper fluidization, thermal cracking and recirculation of particles is extremely slow; and the frequency of procedures, such as withdrawal, pulverization and returning of the particulate heat carrier, required for the regulation of particle size may be reduced, whereby the economy and reliability of the apparatus may be substantially enhanced; thus, it is possible to continuously carry out the process of the invention for a prolonged period of time. Furthermore, since a closed path of the suspension comprising a slurry of cracked oil containing coarse particles of the heat carrier may be formed the process of the invention does not suffer from problems with regard to successful treatment of such a suspension, which is generally extremely difficult to solve.

As already stated, the gravitational separation of coarse particles of the heat carrier may be carried out in the atmospheric pressure distillation column 11 at the bottom thereof without employing a separating vessel. In this modification, measures (e.g. use of a special pump) to counter the deposition of coarse particles of the heat carrier along the path of the oil need only be considered with respect to the system for recycling the oil containing coarse particles densely suspended therein to the reactor 1. No other part of the

apparatus requires a counter measure to the deposition of coarse particles of the heat carrier.

In the known apparatus a reaction column and a cyclone are arranged so that a duct for returning particulate heat carrier collected by the cyclone to the reaction column opens into the reaction column at a position above the level at which the heavy oil feed is fed to the reaction column. In such an arrangement, a pressure balance between the cyclone and the lower end of the particle returning duct as well as that between the lower end of the particle returning duct and the reaction column may be established by the fact that a portion of the cracked gas blows up through the duct. Continued blowing up of the cracked gas inevitably promotes the accumulation of coking materials onto the inner surfaces of the cyclone and duct, whereby the particle returning capacity of the duct is reduced by the narrowing of the path through the duct and the duct collecting efficiency of the cyclone is lowered as well.

It has now been found that such disadvantages may be simply and effectively overcome by arranging the reaction column and the cyclone in such a manner that the upper end of an opening of the particle returning duct to the reaction column is positioned at a level which is below the lower end of an opening for supplying the heavy oil feed to the reaction column by a vertical distance which is equal to the diameter of the opening of the duct to the reaction column or more. The particles of heat carrier which have been returned to the reaction column through the particle returning duct contribute to the regulation of the particle size distribution in the reaction column, admixed with larger particles in the column and upwardly transferred by the fluidizing steam, and utilized in the thermal cracking of the feed oil.

With further reference to FIGURE 2, in a reaction

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column 1 a particulate heat carrier is fluidized by a fluidizing gas 2 which is blown into the column through nozzles provided at the bottom and lower part of the side walls of the reaction column. The particulate heat carrier is heated in a heating column (now shown), passed through a duct 23 to the reaction column 1, where it supplies the required heat of reaction and maintains the required reaction temperature. A heavy oil feed to be thermally cracked is blown through an opening 4 for supplying it into the fluidized bed maintained in the reaction column. The heavy oil is then thermally cracked, a part of it being converted to carbonaceous material which may deposit on the particulate heat carrier while the other part is converted to a cracked gas (most of the cracked products being gaseous at the reaction temperature). It should be noted that the gaseous material, which is present in the upper part of the reaction column above a level at which the heavy oil is fed, comprises the fluidizing gas and the cracked gas, while the gaseous material, which is present in the lower part of the reaction column below a level at which the heavy oil is fed, comprises only the fluidizing gas. Cooled particles of the heat carrier, on to which carbonaceous materials have deposited are passed through a duct 23 to the heating column. When the gaseous material is leaving the surface 29 of the fluidized bed, it carries a quantity of the particulate heat carrier. This is partly because bubbles are formed in the fluidized bed, ascend through the bed and disappear at the surface of the bed whereupon the disappearing bubbles impart some energy to the particles; further particles of smaller size are formed in the fluidized bed due to possible impingement and friction of larger particles against each other and with the inner walls of the reaction column, such particles of smaller size being likely to be accompanied by a stream of the gaseous material leaving the fluidized bed. A portion of the particles of the

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heat carrier may not go beyond a space 30 above the fluidized bed and may return to the bed, while the remaining portion may be withdrawn from the reaction column entrained in the gas.

The gas carrying particles of heat carrier is then passed through a conduit 5 to a cyclone dust collector 6. The gas from which the particles are substantially separated is then withdrawn through a conduit 7 and passed to the subsequent steps, where it is processed in a manner described herein above with reference to FIGURE 1. The particles of heat carrier collected by the cyclone 6 are returned from the cyclone 6 at the bottom 25 thereof, through a particle returning duct 26 with a lower opening 28 to the fluidized bed in the lower part of the reaction column. The main part of the particle returning duct 26 is located outside the reaction column 1 and communicates with the column 1 at a connection 27 below a level at which the lower end of the oil supply opening 4 is located. The opening 28 may be identical with the connection 27, or may project into the fluidized bed as shown by dotted lines. If desired, the lower end of the duct 28 projecting into the fluidized bed may be so designed that it is upwardly deflected. The particle returning duct 26 must be so arranged that the upper end of its opening 28 is positioned at a level which is below the lower end of the oil supply opening 4 by a vertical distance which is equal to the diameter of the opening 28 or more. Although the cracked gas is formed in the upper part of the reaction column 1 above the oil supply opening 4 and in general flows upwardly, a minor portion of the cracked gas may move downwardly owing to diffusion phenomenon. By arranging the opening 28 in the above prescribed manner, the possibility of the existence of the cracked gas in the vicinity of the opening 28 may be practically ignored. The lowest level at which the

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opening 28 may be positioned is not critical. However, the provision of the opening 28 at an excessively low level is not advantageous because a long duct 26 is required.

EXAMPLE 1

CONTROL RUN

An apparatus as shown in FIGURE 1 was used but the gravitational separator 14 was not operated in this control run. A residual oil having a penetration of 80 to 100, which
10 had been obtained by distilling a crude oil, produced in Middle Asia, under a reduced pressure, was supplied to the reactor 1 at a rate of 150 kg/hr. The reactor 1 used was generally cylindrical and had an inner diameter of 600 mm. The oil was cracked at a temperature of 750°C. Fluidizing steam was used in an amount of 380 kg/hr.

The thermal cracking of the oil in the reactor 1 provided 65 Nm³/hr. of a cracked gas, 75 kg/hr. of a cracked oil and 17 kg/hr. of a coke. The loss of coke due to the water gas reaction and that due to the pulverization of the particulate
20 coke was 13 kg/hr. and 3 kg/hr. respectively. The balance of coke at the initial stage was, thus, again of the order of 1 kg/hr. of coke, and, therefore, it was not necessary to externally supply an additional amount of coke. This means the loss of coarse particles of coke, from the cyclone 6, was low. At the initial stage of the operation, the harmonic average of the diameter of coke particles were 0.5 mm and 80% by weight of the total weight of the particulate coke was occupied by particles having a diameter of not more than 0.8 mm. These
30 particle size conditions at the initial stage ensured the desirably smooth fluidization, thermal cracking and particle recirculation. However, as the operation was continued the dust collecting ability of the cyclone 6 was gradually lowered and, at the end

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of a 300 hours continued operation the rate of total loss of coke reached 21 kg/hr. (including the loss of coarse particles of 5 kg/hr., from the cyclone 6), exceeding the rate of formation of coke by 4 kg/hr., and, thus, it became necessary to externally supplement a fresh particulate coke to the system in order to maintain the required volume of the fluidized bed. At that time the average size of coke particles in the fluidized bed was 1.1 mm, and particles having a diameter of not more than 0.8 mm occupied less than 10% by weight of the total weight of the particulate coke. These particle size conditions badly affected the operation of the apparatus, including for example, poor performances of particle recirculation and fluidization, and, thus, it was necessary to frequently carry out procedures for regulating the average size of particles as well as the size distribution of particles in the bed.

RUN ACCORDING TO THE INVENTION

The process described in the Control Run was repeated except that the gravitation separator 14 was operated to recycle the cracked oil containing coarse particles of coke to the reactor. The gravitational separator 14 was operated under the following conditions.

Temperature in the separator 14	160°C
Linear velocity of liquid in the separator 14	5×10^{-3} m/sec.
Terminal velocity of a particulate coke of 0.15 mm in diameter	8×10^{-3} m/sec.
Inner diameter of the separator 14	600 mm
Height of the separator 14	1,500 mm

The process was carried out while returning the cracked oil containing coarse particles of coke to the reactor 1 from the beginning of the operation. It was not necessary at all to supplement any additional amount of coke to the reactor

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1 even after a continued operation for a period of 400 hours. At the end of the period the average diameter of coke particle in the fluidized bed was less than 0.6 mm, and, therefore, no step was required for regulating the particle size distribution.

At the end of the 400 hrs. continued operation the rate of recycle, to the reactor 1, of the oil containing coarse particles of coke was 60 kg/hr. comprising 5kg/hr of coarse particles of coke and 4kg/hr of fine particles of coke. For the transport of the suspension a metering pump was used, so designed that it may not go wrong by the existence of coarse particles of coke, and the deposition of coarse particle in the pipings was avoided by using a linear velocity of liquid through the pipings, of 0.1m/sec. or higher. With respect to curved and branched parts of the pipings special precautions were taken.

At the end of the 400 hours continued operation particle size distribution of the particulate coke in the fluidized bed, of the particulate coke collected by the cyclone 6 and of the particulate coke suspended in the cracked oil, were as noted in Table I below.

20

TABLE I

Particle Size Distribution of
Particles of Coke

Diameter of particle in mm	In reactor in % by weight	In suspension in % by weight	Collected by cyclone in % by weight
> 1.00	16.1	2.6	10.0
0.50 - 1.00	58.3	15.9	54.5
0.15 - 0.50	24.6	37.1	33.4
< 0.15	1.0	44.4	2.1

30

EXAMPLE 2

In this example an apparatus as illustrated in FIGURE 2 was used. The inner diameter of the reaction column 1 used was 600 mm at the part where the space was formed above

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the fluidized bed, and the particle returning duct 26 had an inner diameter of 133 mm. The particle returning duct 25 was connected with the reaction column 1 at a level below the oil supply opening 4. The upper end of the opening of the duct 26 was separated from the lower end of the oil supply opening 4 by a vertical distance of 200 mm. The process was started using a particulate coke having an average diameter of 0.8 mm and steam as a fluidizing gas. The surface of the formed fluidized bed reached a level 1450 mm above the center line of the oil supply opening.

10 A residual oil having a penetration of 80 to 100 which had been obtained by distillating a crude oil, produced in Middle Asia, under a reduced pressure, was supplied to the reaction column 1 at a rate of 150 kg/hr. For better distribution of the oil in the reaction column it was atomized with steam. The combined amount of the fluidizing steam and the atomizing steam employed was 380 kg/hr., using the reaction pressure of $0.1 \text{ kg/cm}^2\text{G}$ at the top of the column 1 and the reaction temperature of 750°C the operation was continued for

20 a period of 410 hours.

In general, the dust collecting ability or efficiency of a given cyclone 6 varies depending upon the particle size of the solid dust to be collected. The larger the dust particles the higher the collecting ability of the cyclone 6. Accordingly, the dust collecting ability of the cyclone 6 may be estimated by determining its collecting ability i.e. the amount of uncollected particles as measured for a dust having a certain relatively large diameter (for example, of a size of at least 0.15 mm).

30 In this example the values of the amount of uncollected particles having a diameter of at least 0.15 mm were determined. The data showed that the amount increased

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with time. The values at the initial stage of the operation and at the end of the operation were 1.0 kg/hr. and 3.0 kg/hr., respectively. From these values, the rate of average increase in the amount of uncollected coarse particles can be calculated as $2.0/410 = 0.009$ kg/hr.

After the 410 hours operation, the cyclone 6 and particle returning duct 26 were dismantled from the apparatus and examined. No deposition of carbonaceous material was observed inside the particle returning duct 26. In the cyclone 6, while no deposition of carbonaceous material was observed at the lower portion thereof (from the bottom up to about one third of the height), at the upper part thereof the inner surface had been uniformly coated with accumulated carbonaceous material of a thickness of about 3 mm.

For comparative purposes, the procedure described above was repeated using an apparatus which was substantially similar to that employed above except for the location of the particle returning duct 26. In the apparatus used the particle returning duct 26 was so arranged that it was passed through the space formed above the fluidized bed in the reaction column and inserted into the bed, as shown in FIGURE 2 with dotted lines. The opening of the particle returning duct 26 was positioned 500 mm below the surface of the fluidized bed. Using the same reaction conditions as in the preceding run the apparatus was operated for a period of 403 hours. The amount of uncollected coarse particles having a diameter of at least 0.15 mm, increased with time, with the initial value of 2.0 kg/hr and the final value of 8.0 kg/hr. From these values, the rate of average increase in the amount of uncollected particles can be calculated as $6.0 / 403 = 0.0149$ kg/hr., which is as high as about three times that obtained in the preceding run. This reveals an intolerable lowering of the dust collecting

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ability of the cyclone 6 due to promoted coking having occurred on the inner surfaces of the cyclone 6 and its dust returning duct 26. In fact, examination of the dismantled cyclone 6 and duct 26 showed that carbonaceous materials had deposited on the outer surface of that portion of the particle returning duct 26, which had been positioned in the reaction column 1, forming an accumulated layer of about 10 mm in thickness, which was likely to be stripped off. Inside the main part of the particle returning duct 26, carbonaceous material had deposited to a thickness of about 2 to 5 mm. Further, inside the cyclone 6 protrusions composed of accumulated carbonaceous materials were observed over the whole surfaces, extending inwardly by length of about 50 to 80 cm.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the thermal cracking of heavy oils with a fluidized bed of a particulate heat carrier comprising forming a fluidized bed of a particulate heat carrier with a heavy oil and steam in a reactor and thermally cracking said heavy oil at a temperature of about 700°C. to about 850°C., the improvement wherein:

a major proportion of the particles of the heat carrier contained in a stream of the reaction product is recovered with a cyclone dust collector for collecting particles of the heat carrier and returned to said fluidized bed;

the remainder of the particles of the heat carrier contained in said stream and which are not recovered by said collector, and which are passed to a processing stage for the reaction product, being allowed to settle under gravity by means of a gravitational separator in a cracked heavy oil;

said cracked heavy oil is separated into two portions, a first portion containing relatively coarse particles of the heat carrier suspended therein and a second portion containing relatively fine particles of the heat carrier suspended therein; and

said first portion of the cracked heavy oil, containing relatively coarse particles of the heat carrier suspended therein, being passed to said fluidized bed.

2. A process in accordance with claim 1, wherein said first portion comprising particles of the heat carrier suspended in said cracked heavy oil, is washed with a light oil prior to being introduced to said fluidized bed.

3. A process in accordance with claim 1 or 2, wherein the collector for collecting particles of the heat carrier is located

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outside the reactor, and the particles of the heat carrier collected by said collector are returned to the reactor at a position which is below a position where the heavy oil is fed to the reactor.

4. A process in accordance with claim 1 or 2, wherein said particulate heat carrier is particulate coke.

5. A process in accordance with claim 1 or 2, wherein said reactor comprises interconnected heating and reaction columns, through which the fluidized particulate heat carrier is recirculated.

6. A process for the thermal cracking of heavy oils to produce olefins comprising:

- (i) forming a fluidized bed of a particulate heat carrier in a reactor,
- (ii) introducing a heavy oil to be cracked into said reactor,
- (iii) thermally cracking said oil in said reactor in the presence of steam at a temperature of 700°C. to 850°C., to produce a cracked reaction product,
- (iv) passing said cracked reaction product containing particles of said heat carrier therein to a cyclone,
- (v) separating a major portion of said heat carrier from said reaction product in the cyclone and returning said major portion to said fluidized bed,
- (vi) passing said reaction product containing the remainder of said heat carrier of step (iv) to a distillation column, and distilling off a lower boiling point fraction

- to leave a higher boiling point fraction containing said remainder of said heat carrier,
- (vii) allowing said remainder of heat carrier to settle under gravity to produce a first portion containing coarse particles of said remainder of said heat carrier therein and a second portion containing five particles of said remainder of said heat carrier therein,
 - (viii) passing said first portion to said fluidized bed in step (i), and
 - (ix) recovering said reaction product from said second portion.
7. A process according to claim 6, wherein said reaction produced in step (v) is quenched to a temperature of 150°C to 350°C prior to entering said distillation column; said first portion in step (vii) contains 5 to 40% by weight of coarse particles of heat carrier suspended therein, said first portion being introduced into said fluidized bed in step (i) at a point below a feed inlet for said heavy oil in step (ii).
8. Apparatus for the thermal cracking of a heavy oil to produce olefins comprising:
- (i) a cracking reactor adapted to maintain a fluidized bed of a particulate heat carrier including first inlet means in a lower portion for steam, second inlet means for feeding heavy oil to said reactor and first outlet means in an upper portion for cracked product,
 - (ii) first conduit means communicating said first outlet means with a cyclone adapted to separate a major portion of particulate heat carrier in said cracked product, and second outlet means in said cyclone for separated heat carrier particles,

- (iii) second conduit means communicating said second outlet means with a third inlet means in said cracking reactor,
- (iv) fourth outlet means in said cyclone and third conduit means communicating said fourth outlet means with separating means including settling means for settling coarse particles of heat carrier contained in said cracked product,
- (v) fifth outlet means in said settling means and fourth conduit means communicating said fifth outlet means with fourth inlet means in said cracking reactor for return of cracked product containing said coarse particles of heat carrier, and
- (vi) sixth outlet means in said settling means for cracked product containing fine particles of heat carrier.

9. Apparatus according to claim 8, wherein said third inlet means in said reactor is below said second inlet means.

10. Apparatus according to claim 9, wherein said separating means comprises a distillation column and said settling means is a gravitational separator, said fourth outlet means communicating with said distillation column, said distillation column having seventh outlet means communicating with said gravitational separator.

11. Apparatus according to claim 10, wherein said third conduit means includes quenching means for said cracked product; and wherein said sixth outlet means communicates with fifth and sixth conduit means, said fifth conduit means communicating with recovery means for said cracked product and being adapted to convey a portion of said cracked product from said sixth outlet means to said recovery means; said sixth conduit means communi-

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cating with fifth inlet means in said quenching means for recycling a portion of said cracked product from said sixth outlet means to said quenching means.

12. Apparatus according to claim 11, wherein said sixth conduit means includes heat exchanger means.

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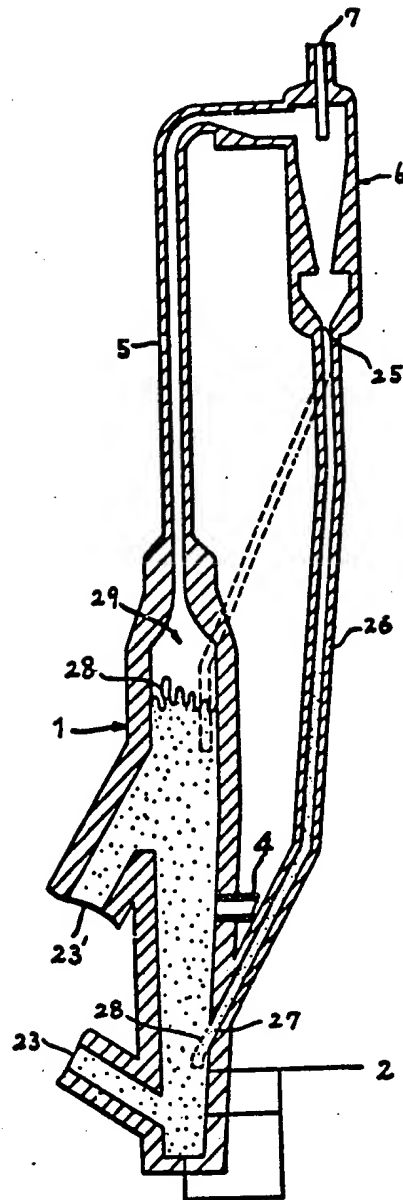


FIG 2

PATENT AGENTS

Allen Sisk & Co.